

MODELLING OF CARBON DIOXIDE ABSORBER USING HOT CARBONATE PROCESS

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by

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to the

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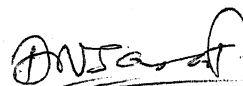
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CERTIFICATE

This is to certify that this work "MODELLING OF CARBON DIOXIDE ABSORBER USING HOT CARBONATE PROCESS" has been carried out by Mr. Dipayan Sanyal under my supervision and it has not been submitted elsewhere for a degree.

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NOMENCLATURE

A_1	Volatile component to be absorbed in the liquid from the gas
A_{ij}	Mixture thermal conductivity parameter
A'	Activity coefficient in VLE relationship
a	Specific wetted area available for mass transfer
a_1	Concentration of A_1 in liquid
a_{1i}	Value of a_1 at the interface
a_{10}	Value of a_1 in the bulk
$a_c, a_d, a_H, a_h, a_s, a', a''$	Regression coefficients
a_d	Specific surface area of dry packing
B	Chemical base
B_j	j th non-volatile reactive species in the liquid
$b_c, b_d, b_H, b_h, b_s, b', b''$	Regression coefficients
b_j	Concentration of B_j in liquid
C	A function of x_c
C_a	Constant
C_i	Concentration of each ionic species
C_{ki}	Concentration of the k th component in the liquid interface
C_{ko}	Concentration of the k th component in the bulk liquid.
C_{Pl}	Average specific heat of CO_2 in the gas phase for the temperature range, 70-135°C

C_{p2}	Average specific heat of water vapour for the temperature range, 70-135°C
C_{pL}	Molar specific heat of liquid
C'_{pL}	Specific heat of liquid
C_{pg}	Molar specific heat of gas
C_R	Average concentration of active component
C'	Constant
$c_c, c_h, c_s,$ c', c''	Regression coefficients
D	Liquid diffusivity
D_{gk}	Diffusivity of kth absorbed component in the gas
D_{kj}	Binary diffusivity in gas
d_h, d', d''	Regression coefficients
d_p	Equivalent packing size
E	Rate promotion factor
E_{max}	Maximum value of E
e_h	Regression coefficient
G	Mass flow rate of inert gas
g	Acceleration due to gravity
H	Henry's law constant in the reactive solution
H_t	Height of the absorption column
H^0	Value of H in pure solvent
ΔH_1	Heat of absorption and reaction of CO_2 with hot potash
ΔH_2	Heat of vapourization of water
h	Coefficient of heat transfer in the gas-liquid interface

h_k	Heat transfer coefficient of kth component
I	Enhancement factor
I_i	Ionic strength of solution
I_{∞}	Value of I in the instantaneous regime
j_D	j factor for mass transfer
j_H	j factor for heat transfer
K_{C_1}	First ionisation constant of carbonic acid
K_{C_2}	Second ionisation constant of carbonic acid
K_{gk}	Overall gas phase mass transfer coefficient of the kth component
K_i, K_m	Constants
K_p	Protonation constant of base B
k_{gk}	Gas phase mass transfer coefficient of kth component
k_L	Chemical mass transfer coefficient in liquid phase
k_{lk}	Liquid phase mass transfer coefficient of kth component
k_L^0	Physical mass transfer coefficient in the liquid phase
k_{II}	Second order reaction rate constant
L	Molar flow rate of liquid
\tilde{L}	Liquid mass flow rate
M	Number of independent chemical reactions
M_g	Average molecular weight of the gas
M_i, M_j	Molecular weight of ith and jth component in the gas
m	Molarity of the liquid solution
m_e	Total amount of amine in solution
N	Absorption flux of A_1 at the interface

N_k	Moles of kth component transferred per unit time per unit length
n	Number of components in the gas mixture
P	Total tower pressure
P_{ki}	Partial pressure of the kth component in the gas at the interface
P_{ko}	Partial pressure of the kth component in the bulk of the gas
p_k^*	Partial pressure of the kth component in the gas phase if it were in equilibrium with the bulk liquid phase
q	Exponent in VLE relationship
dq	Rate of heat generated due to absorption in the differential height, dZ
dq_g	Rate of heat carried by the absorbed component from the gas to the liquid over height dZ
dq_t	Rate of heat transferred from the gas to the liquid due to temperature difference over height dZ
R	Universal gas constant
r	Rate of reaction
r_k	Rate of kth reaction
S	Area of cross-section of the tower
s	Specific gravity of the liquid
T	Gas temperature in K
t	Liquid temperature in K
t_C	Liquid temperature in $^{\circ}\text{C}$
t_F	Liquid temperature in $^{\circ}\text{F}$
V	Molar flow rate of gas

V_k, V_j	Molecular volume of k and j
v	Superficial gas velocity
w	Total equivalent weight percent K_2CO_3
x	Fractional saturation of the liquid
x_c	Fractional conversion of K_2CO_3 to $KHCO_3$
x_k	Mole fraction of the kth component in the liquid phase in unreacted form
y	Distance from the interface towards bulk liquid
y_k	Mole fraction of the kth component in the gas phase
z	Spatial variable along the height of the column
z_i	Charge of each ionic species in solution

Greek Letters

α	Total CO_2 concentration in liquid in both free and combined forms
α_i	Value of α at the interface
α_o	Value of α in the bulk
δ	Film thickness
λ_g	Thermal conductivity of gas
λ_{gi}	Thermal conductivity of pure component i in gas
μ	Liquid viscosity
μ_g	Gas viscosity
μ_{gi}, μ_{gj}	Viscosities of the ith and jth components in the gas
μ_j	Number of moles of A_1 chemically combined with B_j
ρ	Density of the liquid
ρ_g	Density of the gas

ABSTRACT

A mathematical model has been developed for the absorption of carbon dioxide from ammonia synthesis gas in amine promoted hot potassium carbonate solution. The model uses vapour-liquid-equilibrium data for the unpromoted carbonate-CO₂ system which seems to be adequate at low fractional saturation of the liquid with carbon dioxide. In the temperature range of industrial operation, instantaneous reaction rate provides the appropriate enhancement factor for the chemical absorption. The calculated results have been found to be in close agreement with the observed values for an industrial unit. The model has been used to calculate various flow, temperature and concentration profiles in the absorber. Variation of exit CO₂ concentration with some of the operating parameters has also been examined.

CHAPTER 1

INTRODUCTION

For a commercially useful ammonia synthesis process, economic removal of carbon dioxide from the synthesis gas has considerable importance. Carbon dioxide acts as a diluent of the synthesis gas and is also thought to be a poison for the synthesis catalyst when present in large concentration. Industrially, removal of carbon dioxide is largely brought about in two steps. The first step uses an absorption system where a chemical solvent is employed to reduce CO_2 to about 0.1% by volume. In the second step, a catalytic gas-phase methanation reduces total carbon oxides ($\text{CO}_2 + \text{CO}$) to less than 10 ppm, as required to protect the ammonia synthesis catalyst. The first step of the sequence is responsible for bulk removal of CO_2 and hence forms an important part of ammonia synthesis plant. The chemical solvents usually employed in industry are either the amines (e.g., mono-, di-, and triethanolamines) or hot potassium carbonate solution, usually promoted by organic amines. Though amine systems have a greater capacity for carbon dioxide and lower consumption of regeneration steam than the original alkali carbonate process operating at atmospheric pressure, they do not offer any significant advantage at elevated pressures, like the "hot potash" system (Benson et al., 1954). Moreover, hot

potash systems have higher energy efficiency owing to the fact that the heat exchange between the hot and cold streams can be eliminated. These have made the hot potash system evidently popular over the amine systems. Among the processes employing hot potassium carbonate as the basic chemical solvent, namely, the Benfield process, the Giammarco-Vetrocoke process, the Catacarb process and so on (Slack and James, 1974; Kohl and Risenfield, 1979; Strelzoff, 1981) the former has gained the broadest industrial acceptance for acid gas removal. The original Benfield process, developed at the U.S. Bureau of Mines in the early 1950s (Benson et al., 1954, 1956; Field et al., 1962) by Benson, Field and co-workers with a view to economically remove CO_2 and H_2S at high pressure from coal derived synthesis gas, has undergone several major modifications (Parrish and Neilson, 1974; Bartoo and Ruzicka, 1983; Bartoo, 1984), all geared towards decreasing the investment costs and the utilities requirements while, at the same time, enhancing operational reliability and flexibility. At present, there are over 520 installations throughout the world using the Benfield process with various modifications (Bartoo, 1984) and this indeed speaks for itself, the need to model the Benfield absorption system, more than any other system, as an integral part of an Ammonia plant Flowsheeting programme. A separate, yet concise, discussion on the Benfield system, relevant to present work, is therefore given in Chapter 2.

The most important aspect of the Benfield system, that discerns it from other absorption systems is that the absorption of carbon dioxide is accompanied and enhanced by simultaneous chemical reaction with potassium carbonate. This makes the problem of modelling the system quite involved and prone to cumbersome calculations. Though the theory of chemical absorption was established in the late 60s (Danckwerts, & Sharma, 1966; Astarita, 1967; Ramm, 1968) adequate vapour-liquid equilibrium (VLE) data and the kinetics of reaction with concentrated hot potash solution, particularly, for the high temperature range usually employed by the industry, were still not to be found in the open literature. Most of the data were proprietary and well beyond the reach of the scientists in the open world. Moreover, the effect of various organic promoters on the kinetics and VLE curve were not known in its entirety. All these had contributed to making the modelling of Benfield absorber a difficult, though not impossible, proposition. In early 70s, Uchida et al. (1972) published a rather simplistic "compartment-in-series" model for design and simulation of an adiabatic packed absorber, which was tested for the case of CO_2 absorption in hot potash solution. The thermodynamics and kinetics developed for the problem were anything but rigorous. Apart from this a computer program for design of hot carbonate absorption system was published by (Wellman and Katell (1968). No mathematical model, however, was presented

alongwith the package. Availability of recent accurate thermodynamic (Kent and Eisenberg, 1975; Astarita et al., 1983) and kinetic data (Astarita et al., 1983) as well as knowledge of the effects of rate promotion (Astarita et al., 1981; 1983) and other information related to this system, has paved the way for attempting simulation of the Benfield absorbers.

The mathematical modelling of the Benfield absorbers with the relevant thermodynamic and kinetic models has been described in Chapter 3. The packed absorber has been modelled on the basis of two-film theory of mass transfer which for all practical purposes can be deemed at least as good as the more sophisticated penetration or surface renewal models (Astarita, 1967). Other relevant parts of the model have been developed primarily on the basis of the theoretical analysis of Astarita et al. (1983). Recently published thermodynamics data and transport properties have been incorporated in the present model in the form of suitable correlations obtained either directly from literature or by means of regression analysis of available curves. The two-point boundary value problem, generated from the steady state heat and material balance around a differential section of the packed absorber has been solved by the shooting method (Fox, 1957). The model developed in the present work has been validated with plant data. The fourth chapter presents a discussion of the results and gives the profiles

of flow rates, temperature and composition along the tower height for the gas and liquid streams. The implications of these and the scope of future modifications have been included in Chapter 5. A User's Manual for the computer program has been provided as an Appendix B. Program listing is given in Appendix C.

CHAPTER 2

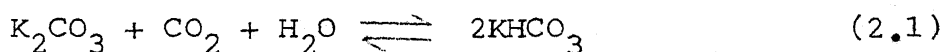
THE BENFIELD PROCESS

2.1 Process Description

Historically, the development of the famous "Benfield" process, named after its discoverers Benson and Field of U.S. Bureau of Mines, was stimulated in the early 1950s, by the urge of finding an improved method of removing carbon dioxide from Fischer-Tropsch synthesis gas which would reduce the high capital and operating costs (Field et al., 1962). Since, coal, oxygen and steam are reacted under high pressure, at about 20 to 35 atm. in that process, it is more economical to use the absorption system at elevated pressure than at the atmospheric to eliminate a subsequent compression system for gases. This holds equally good for ammonia synthesis gas which reacts under high pressure (15 to 25 atm) in the synthesis reactor. In order to exploit the advantage of the elevated pressure and temperature at which the impure gases are available, the use of hot concentrated alkaline solutions under pressure was investigated by the U.S. Bureau of Mines. In this system, the driving force which is the difference between the partial pressure of carbon dioxide in the bulk of the gas and its equilibrium partial pressure at the gas-liquid interface, was believed to be sufficient for absorption without the conventional lowering of temperature. Contrary to the usual practice,

absorption would then be possible at about the same temperature as regeneration. Since the carbonate-bicarbonate solution remains hot at all times, more concentrated solutions can be used than with cold absorption without precipitating the bicarbonate (Benson et al., 1954; 1956).

Since a high concentration of alkalinity was desirable, potassium carbonate was considered to be more suitable than the sodium salt because the solubility of potassium bicarbonate was much greater than that of sodium bicarbonate. The bicarbonate is formed during absorption according to the following overall reaction



Moreover, at normal temperature, the equilibrium partial pressure of carbon dioxide over solution of potassium carbonate was lower than that for comparable concentration of sodium salt solution. Hence potassium carbonate was again preferred to sodium carbonate (Harte, et al., 1933). Figure 2.1 shows a simplified flowsheet for the potassium carbonate process. The absorber operates at an elevated pressure of about 25 atm and the regenerator at about 1 atm. The lean carbonate solution flows from the bottom of the regenerator and is pumped, without cooling, to the top of the absorber. The rich solution leaving the bottom of the absorber flows to the top of the

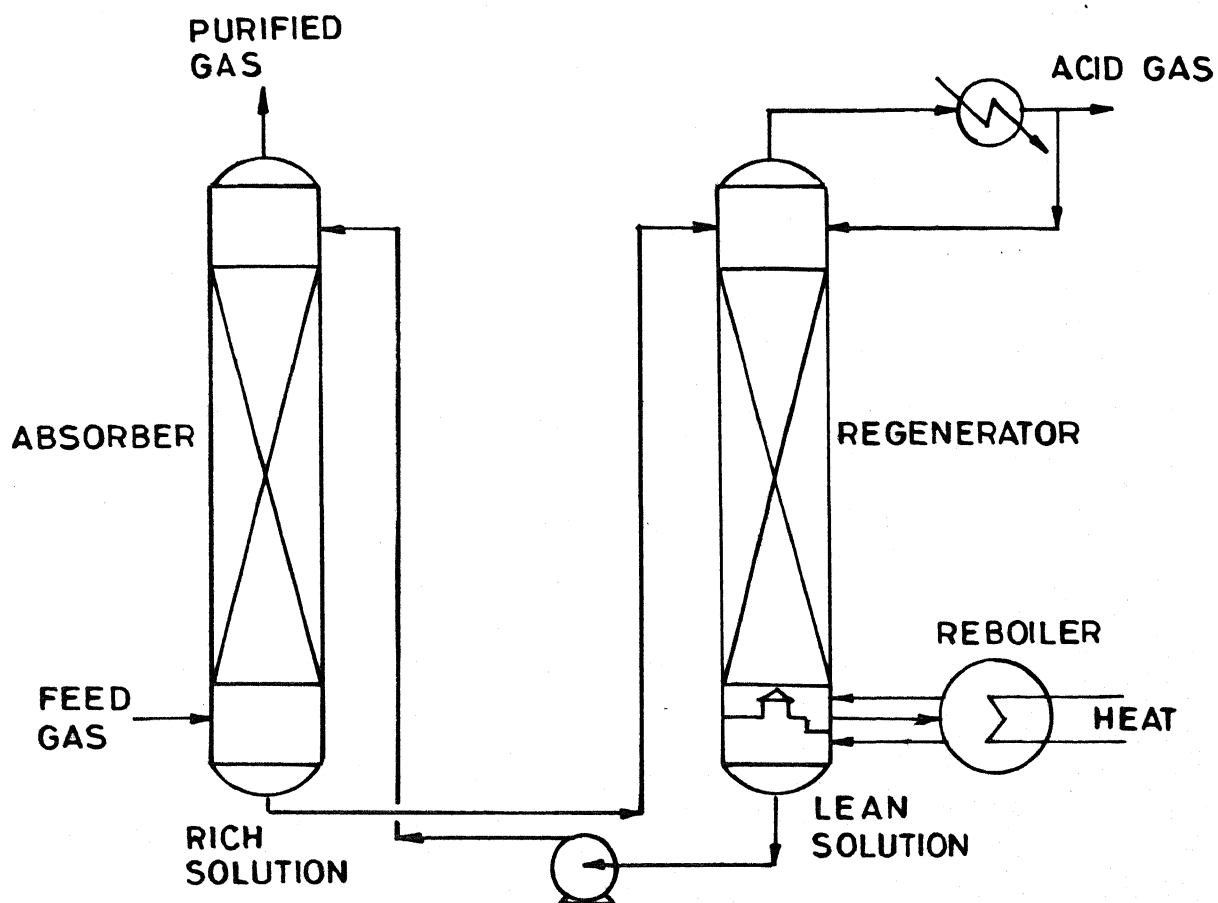


Fig. 2.1 Simplified flow-sheet of single-stream absorber

regenerator after pressure let down. Some dissolved carbon dioxide and steam are flashed from the depressurized solution, but the rest of the carbon dioxide is stripped by steam produced by boiling the solution in the reboiler. The typical temperature of the rich solution leaving the absorber ranges from about 105 to 120°C, whereas the lean solution is at about 120-125°C. In the scheme shown in Figure 2.1, only single stream flows both in the absorber and the regenerator. This is generally used for carbon dioxide removal to a typical purity of 1% CO₂.

For a higher degree of purification, the flowscheme shown in Figure 2.2(a), a "Split-flow absorber" design is used. The bulk of the hot, regenerated lean solution, 60% - 70% of the total, is introduced into the absorber at an intermediate point, while a small trim solution is cooled by 10°-40°C and pumped to the top of the tower. The lower temperature trim stream has a reduced equilibrium back pressure of carbon dioxide to permit attaining high purity of 0.1% CO₂ in the purified gas. Since the bulk of the absorber still operates at high temperature, the rich solution stream is hot and regeneration efficiency is not impaired (Bartoo, 1984).

When still higher purity is required, a "two-stage" design, i.e., a split-stream flow in the absorber and split-stream flow in the regenerator is required (Figure 2.2(b)).

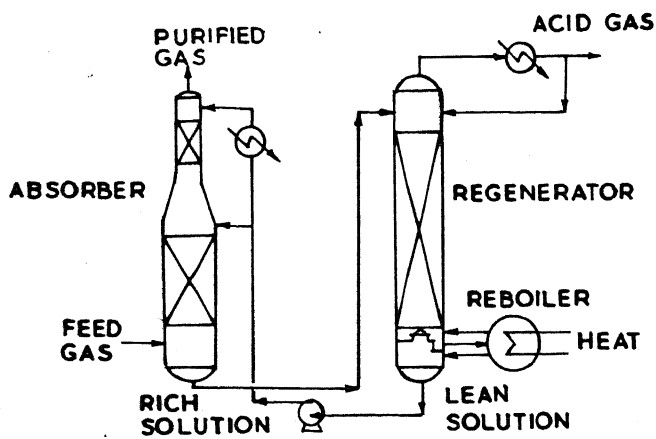


FIG. 2.2(a)

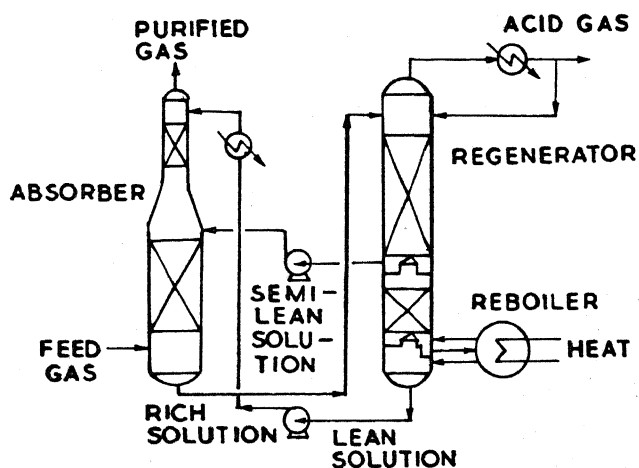


FIG. 2.2(b)

Fig. 2.2 (a) Simplified flowsheet of cooled split-flow absorber

2.2 (b) Simplified flowsheet of split-flow absorber with two stage regenerator

Two regenerated streams leave the regenerator; the major portion (60-85% of the total) is removed from an upper level in a partially regenerated state for return to an intermediate level of the absorber. The minor stream, 15-40% of the total is regenerated further in the bottom section of the regenerator by the total boil up steam, removed from the sump, and cooled before being pumped to the top of the absorber. In this scheme, the CO₂ level in the purified gas is brought down to 0.05%. The CO₂ cleanup attainable with the various flowsheet configurations described above is summarized in Table 2.1.

Table 2.1: CO₂ Cleanup Attainable with Promoted Hot Carbonate Process(*)

Configuration	Final CO ₂ content
Single stream absorber	1% or greater
Cooled split flow absorber	0.1 - 1%
Cooled split flow absorber and two-stage regenerator	500-1000 ppm

(*) Astarita, Savage & Bisio; Gas Treating with Chemical Solvents, 1983

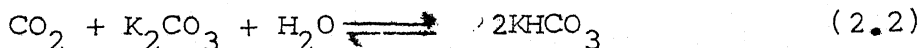
Recently other improvements over these conventional schemes have been proposed (Parrish and Neilson, 1974; Bartoo and Ruzicka, 1983; Bartoo, 1984) for example, the Hipure & Loheat Processes. The Hipure process employs two independent

solution circuits, arranged to have multiple use of the regeneration steam from the secondary circuit. The Loheat process recovers heat internally by reducing pressure over the regenerated lean solution and compressing the steam flashed off.

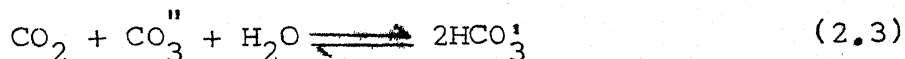
For further details about various gas treating processes, the reader is advised to refer to "Ammonia" by Slack and James (1974), "Gas Purification" by Kohl and Risenfeld (1979), "Technology and Manufacture of Ammonia" by Strelzoff (1981), and "Gas Treating with Chemical Solvent" by Astarita et al. (1983).

2.2 Chemistry of the Process:

When carbon dioxide is absorbed in an unpromoted solution of potassium carbonate and bicarbonate, it reacts according to the following overall reaction

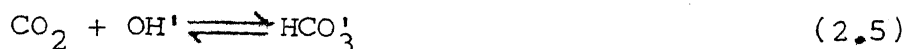
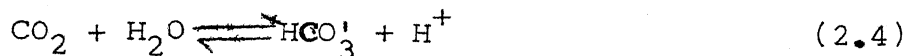


Since potassium carbonate and bicarbonate are both strong electrolytes, it may be assumed that the metal is present only in the form of K^+ ions, so that the reaction (2.2) may be more realistically represented in the ionic terms as

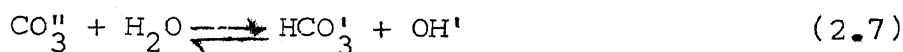


In absorption, reaction 2.3 proceeds from left to right. The above reaction, being trimolecular, is evidently made up of a sequence of elementary steps. Carbon dioxide may undergo

two direct reactions in an alkaline solution, namely



Both reactions (2.4) and (2.5) are followed by an instantaneous reaction leading to the overall result developed by reaction (2.3).



Both these reactions are accompanied with the following instantaneous dissociation reaction



The first sequence, namely, reactions (2.4), (2.6) and (2.8) is known as the "acidic" mechanism by Wall (Savage et al., 1980). The acidic mechanism's contribution to the overall reaction rate is negligible unless the pH of the liquid solution is very low. Almost all the cases of industrial absorption are held at high pH ($\text{pH} > 8$) and hence the acidic mechanism is neglected altogether in the present study. Since reactions (2.7) and (2.8) are instantaneous reactions, reaction (2.5) is the rate controlling step for absorption of CO_2 in unpromoted hot potash solution.

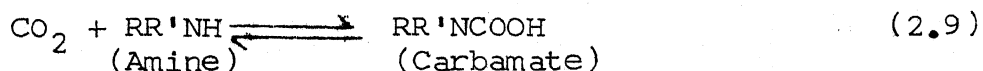
2.3 Chemistry of Rate Promotion:

Though significant rate enhancement is observed for the K_2CO_3 system of temperatures exceeding 318 K, the rate of chemical reaction is still not large enough, even at temperatures as high as 378 K, for the reaction to be regarded as instantaneous (Savage et al., 1980). Therefore, even at the highest temperatures of industrial practice the use of additives for rate promotion is of significant interest.

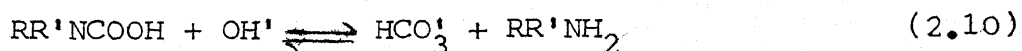
Promotion of mass transfer rates, through additives to the K_2CO_3 solution, has been reported in the literature (Shrier and Danckwerts, 1969; Roberts and Danckwerts, 1962; Danckwerts and Sharma, 1966; McLachlan and Danckwerts, 1972; McNeil and Danckwerts, 1964, 1967; Jeffreys and Bull, 1964; Astarita and Beek, 1962). The most recent theory has been discussed by Astarita et al. (1981). It is assumed that the role of additives is that of a catalyst in the reaction rather than a modifier of vapor-liquid equilibrium. Two main types of additives have been studied, inorganic and organic; both of which have been used commercially. Among the inorganic additives, arsenious acid and among the organic additives, ethanolamines exhibit large promotional effects.

The absorption rate promotion by amines has been explained in terms of the so called "Shuttle Mechanism" by Astarita et al. (1981). In the region near the gas-liquid

interface, CO_2 is assumed to dissolve and undergo a fast reaction with free amine resulting in the formation of carbamate. This reaction is fast enough to steepen, significantly, the CO_2 concentration profile, and therefore to enhance the mass transfer rate. Figure 2.3 shows a qualitative diagram describing the 'shuttle mechanism'. The reversion of the carbamate ion to bicarbonate ion is known to be a slow reaction. Therefore, to react significantly, the carbamate ion must diffuse to the bulk of the liquid phase, where it reverts to bicarbonate and liberates free amine. The free amine then diffuses back to the interface region where it can react again with carbon dioxide. The overall reaction for CO_2 absorption is still eqn.(2.5). But, for rate promotion with the help of amino compounds, the reaction is



Reversion of the carbamate to bicarbonate ion takes place in the bulk of the liquid as follows:



The sequence of reactions given by Eqs. (2.9) and (2.10) can be considered as "homogeneous catalysis mechanism" or "shuttle mechanism" according to the relative rate of reaction (2.10) with respect to (2.9). For the "homogeneous catalysis mechanism" reaction (2.10) is so much faster than (2.9) that

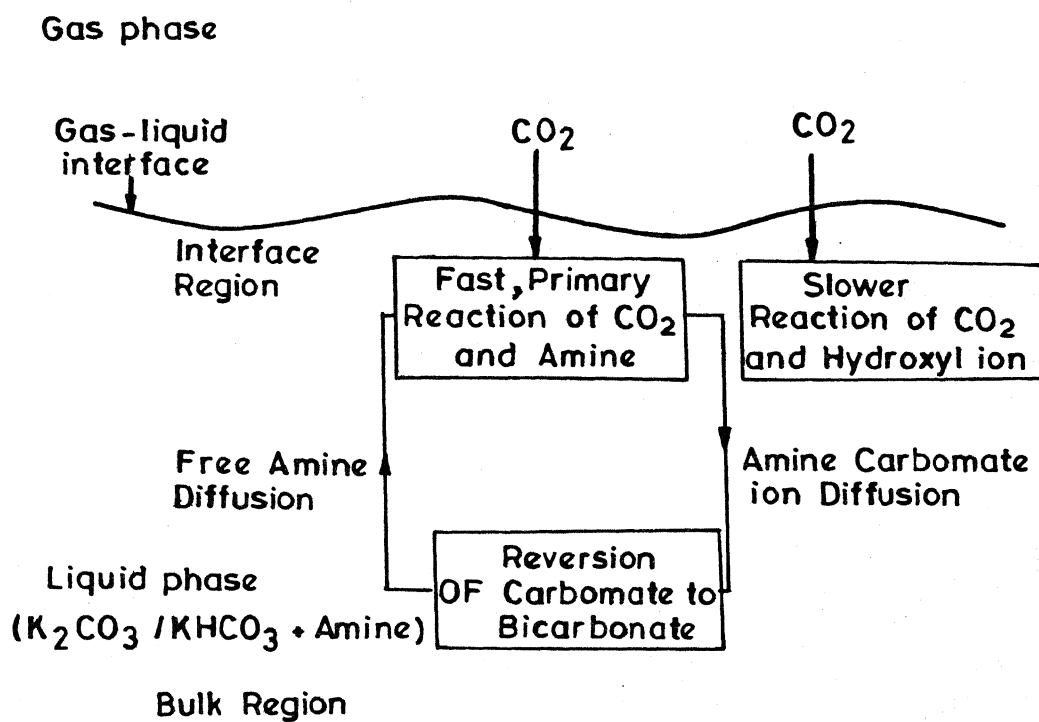


Fig. 2.3 Shuttle mechanism for absorption in amine-promoted carbonate solution

it follows the latter immediately and locally. For the shuttle mechanism, however, the reverse is true, i.e. reaction (2.10) is much slower than (2.9) and the reaction takes place in the bulk of the liquid. At room temperature, the relative rates of the two reactions are such that the shuttle mechanism is operative. However, at higher temperatures, in the range of industrial operation, the rate of reaction (2.10) increases significantly and the system is better represented by the homogeneous catalysis mechanism. This mechanism shoots up the overall reaction rate to instantaneous regime. The kinetics of rate promotion step will be discussed later (Section 3.5).

CHAPTER 3

MATHEMATICAL MODELLING OF HOT CARBONATE ABSORBER

Since chemical absorption is the basic mechanism of acid gas absorption in the Benfield process, the relevant theory will be discussed briefly. The phenomenon of gas absorption in a liquid with simultaneous chemical reaction has been studied extensively over the last three decades through wide experimentation as well as theoretical analysis. But it was only in the late 60s, that Ramm (1968); Astarita (1967) and Danckwerts & Sharma (1966) published these information in a collected, coherent fashion. Since then many works have followed (Leder, 1971; Savage et al., 1980; Astarita and Savage, 1980; Astarita et al., 1981 etc.) and the most recent analysis and information are available in the treatise by Astarita et al. (1983).

3.1 General Background:

For the present analysis, we focus attention on a system consisting of a chemical solvent used for absorbing one component from a gas stream. Let A_1 be the component to be absorbed which can be present both in gas phase and liquid phase. All other components of the gas stream are regarded as non-condensable except water vapor. The components present

in the liquid stream are considered to be non-volatile except water and the solute A_1 . Further analysis is based on two important terms, molarity of the chemical solvent and the degree of saturation or fractional saturation. Molarity, m , is the total equivalent concentration of the species that may react equimolarly with component A_1 . It is also the actual concentration of the reactive species that could be attained in the chemical solvent if, in the desorption unit, all chemically combined A_1 could be stripped from the solvent. The degree of saturation or fractional saturation, x , is defined as the ratio of the concentration of the absorbed component to the total concentration of the reactive component in both reacted or unreacted forms.

The reactions between A_1 and B_j , the non-volatile reactive species in the liquid can be expressed as

$$A_1 + \sum v_{jk} B_j = 0 \dots\dots (k = 1, 2, \dots, M) \quad (3.1)$$

where M is the total number of independent chemical reactions.

The stoichiometric coefficient v_{jk} of the j th non-volatile components in k th reaction are not independent of each other and obey the following equation for preservation of atoms in a chemical reaction

$$1 + \sum v_{jk} \mu_j = 0 ; \quad k = 1, 2, \dots, M \quad (3.2)$$

v_{jk} is positive if a component is a reactant, negative if it is

a product and zero if it is inert. μ_j represents the number of moles of A_1 which are present in chemically combined form in component B_j (Astarita and Savage, 1980).

For the case of unpromoted CO_2 - K_2CO_3 system there is only one overall reaction ($M=1$) and there are four species to be considered namely $A_1 = \text{CO}_2$ (the volatile component), $B_1 = \text{OH}^+$, $B_2 = \text{CO}_3^{2+}$ and $B_3 = \text{HCO}_3^+$ (the non-volatile components). The stoichiometric coefficient of B_j and the number of moles of A_1 chemically combined with B_j , denoted by ν_j and μ_j respectively are given as follows:

$$\begin{array}{lll} \text{OH}^+ : & \nu_1 = 0 & , \mu_1 = 0 \\ \text{CO}_3^{2+} : & \nu_2 = 1 & , \mu_2 = 1 \\ \text{HCO}_3^+ : & \nu_3 = 2 & , \mu_3 = 1 \end{array} \quad (3.3)$$

The total concentration of CO_2 in the liquid phase in free and combined forms; denoted by α , is given by

$$\alpha = a_1 + \sum_i \mu_i b_i = a_1 + b_2 + b_3 \quad (3.4)$$

where a_1 , b_2 and b_3 are the concentration of the species A_1 , B_2 and B_3 respectively in the liquid phase.

The liquid phase composition of absorbed component described by fractional saturation, x , is given as follows:

$$x = \frac{b_3}{2m} \quad (3.5)$$

where m is the molarity, i.e., the total K_2CO_3 concentration

$$m = [K^+] / 2 = (2b_2 + b_3) / 2 \quad (3.6)$$

where $[K^+]$ is the potassium ion concentration.

From (3.4), (3.5) and (3.6) we obtain:

$$\alpha = a_1 + m(1+x) \quad (3.7)$$

If r_k is the rate at which the k th reaction is taking place (for absorption r_k is positive and for desorption it is negative) then film theory differential equations for diffusion reaction are

$$\frac{d^2 a_1}{dy^2} = \sum_k \frac{r_k}{D} \quad (3.8)$$

and

$$\frac{d^2 b_j}{dy^2} = \sum_k \nu_{jk} \frac{r_k}{D} \quad (3.9)$$

where y is the distance from the interface towards bulk liquid and D is the liquid diffusivity, assumed to be same for all components. Differentiating equation (3.4) twice with respect to y and substituting in equations (3.8) and (3.9) the following equation is obtained:

$$\frac{d^2 \alpha}{dy^2} = \sum_k \left[\frac{r_k}{D} \left(1 + \sum_y \mu_j \nu_{jk} \right) \right] \quad (3.10)$$

In view of equation (3.2), Eq.(3.10) reduces to

$$\frac{d^2 \alpha}{dy^2} = 0 \quad (3.11)$$

Equation (3.11) implies that the profile of α through the film is linear and therefore

$$\left. \frac{d\alpha}{dy} \right|_i = \frac{\alpha_o - \alpha_i}{\delta} \quad (3.12)$$

where suffixes i and o refer to the interface and bulk liquid conditions respectively and δ is the thickness of the film.

The physical mass transfer coefficient k_L^o is related to δ as

$$k_L^o = \frac{D}{\delta} \quad (3.13)$$

Since B_j s are non-volatile, their flux at the interface, when all diffusivities are equal, is zero, i.e.,

$$\left. \frac{db_j}{dy} \right|_i = 0 \quad (3.14)$$

Combining equations (3.4), (3.12) and (3.14) we arrive at

$$\left. \frac{da_1}{dy} \right|_i = \frac{\alpha_o - \alpha_i}{\delta} \quad (3.15)$$

If N is the absorption flux of A_1 at the interface, then by definition

$$N = -D \left. \frac{da_1}{dy} \right|_i \quad (3.16)$$

Equation (3.13), (3.15) and (3.16) when combined yield,

$$N = k_L^o (\alpha_i - \alpha_o) \quad (3.17)$$

A "chemical" mass transfer coefficient is customarily defined as

$$N = k_L (a_{1i} - a_{1o}) \quad (3.18)$$

Comparing equations (3.17) and (3.18), we arrive at an important concept of enhancement factor, I , defined as, the ratio of the

actual rate and the rate that would be observed under the same driving force in the absence of chemical reactions

$$I = \frac{k_L}{k_L^0} = \frac{\alpha_i - \alpha_o}{a_{1i} - a_{1o}} \quad (3.19)$$

In the classical chemical absorption theory, four asymptotic regimes have been identified; the kinetic (KR), diffusional (DR), fast reaction (FR) and instantaneous reaction (IR) regimes (Astarita, 1967). There are, however, transition regimes like kinetic-diffusional, diffusional-fast, etc.

The value of the enhancement factor will depend on the particular regime controlling the chemical absorption of CO_2 . For reasons to be described, in detail, later in this chapter (Section 3.5), we focus attention on the instantaneous reaction regime. Physically, instantaneous regime is the case where the chemical reactions are so fast that chemical equilibrium prevails at all points in the liquid phase and therefore the chemical reactions take place at whatever rate the reactants are brought together by diffusion. Quite obviously the instantaneous regime represents an upper band, since all resistance to absorption (or desorption) rate due to chemical kinetics has been reduced to zero. Though Savage et al. (1980) have given a mathematical expression of the enhancement factor, I , for the instantaneous regime, it is still not easy to calculate the above quantity as one is required to know

the interfacial compositions of A_1, B_2, B_3 etc., which in practical cases, are very difficult to find. Van Krevelen and Hoftijzer (1948) developed an expression for the enhancement factor which was basically the Hatta number, defined as

$$I = \frac{\left(\frac{\mu^2}{g \rho^2}\right)^{1/3} \left(\frac{k_{II} C_R}{D}\right)^{1/2}}{\tanh \left(\frac{\mu^2}{g \rho^2}\right)^{1/3} \left(\frac{k_{II} C_R}{D}\right)^{1/2}} \quad (3.20)$$

where μ = viscosity of liquid, Kg/(m)(hr)

ρ = density of liquid, Kg/m³

g = acceleration due to gravity, m/(hr)²

k_{II} = second-order reaction rate constant, Km³/(m³)(hr)

C_R = average concentration of active component, Km³/m³

This equation is simple to use and the sophisticated analysis of Astarita and Savage (1980) according to the authors themselves, have improved very little over the results of the above equation (3.20). Estimation of k_{II} is given in Appendix A.

3.2 Material and Energy Balances:

The material and energy balance equations have been developed on the basis of the two-film model of mass transfer proposed by Whitman (1923). The equation for the flux N_k , moles of k th component transferred per unit time per unit length of the absorber can, therefore, be written as

$$\begin{aligned}
 N_k &= (k_{gk}a) (p_{ko} - p_{ki})(S) = (k_{lk}a)(C_{ki} - C_{ko})(S) \\
 &= (k_{gk}a) (p_{ko} - p_k^*)(S)
 \end{aligned}
 \tag{3.21}$$

where k_{gk} = gas phase mass transfer coefficient of the k th component, $\text{Kmol}/(\text{hr})(\text{m}^2)(\text{atm})$

k_{lk} = liquid phase mass transfer coefficient of the k th component, $\text{Kmol}/(\text{hr})(\text{m}^2)(\text{Kmol}/\text{m}^3)$

a = wetted area available for mass transfer, m^2/m^3

p_{ko} = partial pressure of component k in the bulk of the gas, atm

p_{ki} = partial pressure of component k in the gas at the interface, atm

C_{ko} = concentration of component k in the bulk liquid, Kmol/m^3

C_{ki} = concentration of component k in the liquid interface, Kmol/m^3

S = area of cross-section of the packed tower, m^2

p_k^* = partial pressure of the k th component in the gas phase if it were in equilibrium with the bulk liquid phase, atm.

In spite of its simplicity, the two-film model, for all practical purposes, is a reasonably accurate model. Astarita and Savage (1980) have observed that the film theory solution not only gives a very reasonable first-order approximation but

also coincides with the solution obtained from the more sophisticated penetration theory model when all diffusivities are equal.

The material and energy balance equations are developed around a differential height of the packed absorber shown in Fig.3.1. Envelope III is an elemental volume in the differential packed height, dZ , of the absorber, consisting of the gas and liquid films denoted by envelopes I and II respectively. N_1, N_2 are the mass fluxes of the components and dq_g, dq_t and dq_l are the different heat fluxes at the gas-liquid interface separating envelopes I and II. The major assumptions are:

1. The pressure drop through the bed is negligible.
2. Steady state conditions prevail.

Overall mass balance on envelope III:

$$\frac{dL}{dZ} = \frac{dV}{dZ} + r \quad (3.22)$$

where r = rate of reaction, $\text{kmol}/(\text{m}^3)(\text{hr})$

L = molar flow rate of liquid, kmol/hr

V = molar flow rate of gas, kmol/hr

Z = spatial variable along the height of the absorption column, m

Overall mass balance on envelope I:

$$\frac{dV}{dZ} = - \sum N_k = -(N_1 + N_2) \quad (3.23)$$

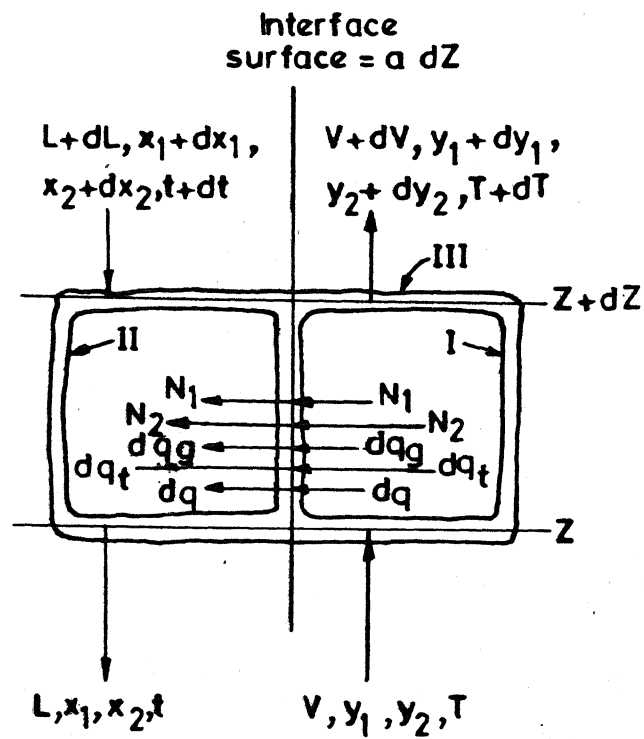


Fig. 3.1 Differential section of a packed absorber

In the present case, carbon dioxide and water vapour are the two components in the gas phase that are absorbed in (or desorbed from) the liquid phase. Therefore $\sum N_k$ consists of N_1 , the molar flow rate of carbon dioxide per unit time per unit length and N_2 , the molar flow rate of water vapour per unit time per unit length.

Component balance on envelope III:

$$\frac{d(Lx_k)}{dz} = \frac{d(vy_k)}{dz} + rS \quad (3.24)$$

which for the present case yields

$$\frac{d(Lx_1)}{dz} = \frac{d(vy_1)}{dz} + rS \quad (3.25)$$

and

$$\frac{d(Lx_2)}{dz} = \frac{d(vy_2)}{dz} + rS \quad (3.26)$$

where x_k = mole fraction of the kth component in the liquid phase in unreacted form

y_k = mole fraction of the kth component in the gas phase.

Suffixes 1 and 2 denote carbon dioxide and water vapour, respectively.

Component balance on envelope I:

$$\frac{d(vy_k)}{dz} = -N_k \quad (3.27)$$

Equation (3.27) gives rise to the following equations for the present case,

$$\frac{d(vy_1)}{dz} = -N_1 \quad (3.28)$$

$$\frac{d(vy_2)}{dz} = -N_2 \quad (3.29)$$

Combination of the equations (3.23) and (3.28) gives

$$\frac{dy_1}{dz} = \frac{N_2 y_1 - N_1 (1 - y_1)}{V} \quad (3.30)$$

Similarly equations (3.23) and (3.29) yield

$$\frac{dy_2}{dz} = \frac{N_1 y_2 - N_2 (1 - y_2)}{V} \quad (3.31)$$

Again, combination of equations (3.22), (3.23), (3.25) and (3.28) gives

$$\frac{dx_1}{dz} = \frac{(rs - N_1)(1 - x_1) + x_1 N_2}{L} \quad (3.32)$$

Similarly, from equations (3.22), (3.23), (3.26) and (3.29), one arrives at the following equation

$$\frac{dx_2}{dz} = \frac{(rs - N_2)(1 - x_2) + x_2 N_1}{L} \quad (3.33)$$

The energy balance of the packed absorber is done on the consideration that it operates under adiabatic condition

Heat balance on envelope II:

By making energy balance for the liquid side around the differential tower height and taking help of equation (3.22)

one arrives at

$$\frac{dt}{dz} = \frac{(N_1 + N_2 - rS)t}{L} - \frac{1}{L C_{pL}} \left(\frac{dq_g}{dz} \right) - \frac{1}{LC_{pL}} \left(\frac{dq_t}{dz} \right) - \frac{1}{LC_{pL}} \left(\frac{dq}{dz} \right) \quad (3.34)$$

where dq_g = rate of heat carried by the absorbed components from gas phase to liquid phase over the differential height, dz .

$$= (N_1 C_{p1} + N_2 C_{p2}) dz T, \text{ Kcal/hr} \quad (3.35)$$

where C_{p1} and C_{p2} are the average specific heats of carbon dioxide and water respectively in the gas phase and C_{pL} is the average specific heat of the liquid. The values of C_{p1} and C_{p2} are 8.1072 and 9.9023 Kcal/(Kmol)(K), respectively.

dq_t = rate of heat transferred from gas phase to liquid phase in the differential section of the tower due to temperature difference over the differential height, dz

$$= h a dz \cdot S(T-t), \text{ Kcal/hr} \quad (3.36)$$

where h = coefficient of heat transfer in the gas-liquid interface, Kcal/(m²)(hr)(K)

T = temperature of the gas phase, K

t = temperature of the liquid phase, K

dq = rate of heat generated due to absorption in the differential height dz of the tower

$$= (rS \Delta H_1 + N_2 \Delta H_2) dz, \text{ Kcal/hr} \quad (3.37)$$

where ΔH_1 = heat generated due to reaction of carbon dioxide with hot potash, Kcal/Kmol

ΔH_2 = heat of vapourisation of water, Kcal/Kmol

Incorporating the expressions for dq_g , dq_t and dq (equations (3.35), (3.36) and (3.37)) in equation (3.34) one arrives at

$$\frac{dt}{dz} = \frac{(N_1 + N_2 - rS)}{L} - \frac{(N_1 C_{p1} + N_2 C_{p2})T}{LC_{pL}} - \frac{haS(T-t)}{LC_{pL}} - \frac{rS \Delta H_1 + N_2 \Delta H_2}{LC_{pL}} \quad (3.38)$$

Heat balance on envelope I:

The gas phase differential heat balance equation is given as,

$$\frac{dT}{dz} = \frac{(N_1 + N_2)T}{V} - \frac{1}{VC_{pg}} \left(\frac{dq_g}{dz} \right) - \frac{1}{VC_{pg}} \left(\frac{dq_t}{dz} \right) \quad (3.39)$$

Combining equations (3.35), (3.36) and (3.39) one gets

$$\frac{dT}{dz} = \frac{(N_1 + N_2)T}{V} - \frac{(N_1 C_{p1} + N_2 C_{p2})T}{VC_{pg}} - \frac{haS(T-t)}{VC_{pg}} \quad (3.40)$$

The change in compositions of K_2CO_3 and $KHCO_3$ are related to the change in CO_2 composition according to the stoichiometry of the overall reaction (2.2). For the special case of instantaneous reaction regime, where chemical reaction takes place at the same rate at which the reactants are brought together by diffusion, $N_1 = rS$ and equations (3.22), (3.32), (3.33) and (3.38) will take the forms as follows

$$\frac{dL}{dz} = -N_2 \quad (3.41)$$

$$\frac{dx_1}{dz} = \frac{x_1 N_2}{L} \quad (3.42)$$

$$\frac{dx_2}{dz} = \frac{N_1 - N_2(1-x_2)}{L} \quad (3.43)$$

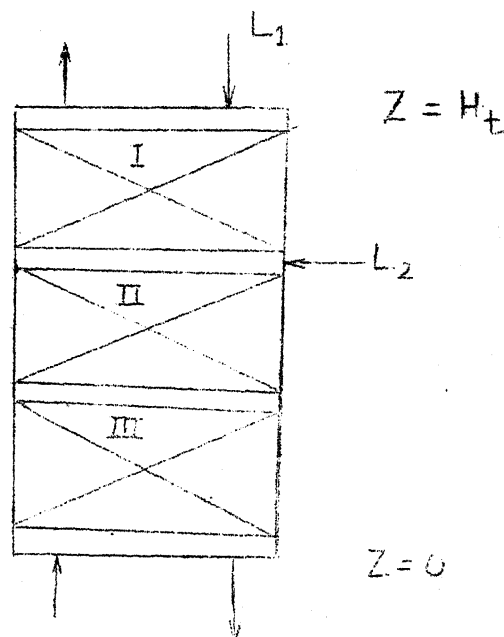
and

$$\frac{dt}{dz} = \frac{N_2 t}{L} - \frac{(N_1 C_{p1} + N_2 C_{p2})T}{LC_{pL}} - \frac{haS(T-t)}{LC_{pL}} - \frac{N_1 \Delta H_1 + N_2 \Delta H_2}{LC_{pL}} \quad (3.44)$$

Equations (3.23), (3.30), (3.31), (3.40), (3.41), (3.42), (3.43) and (3.44) form the model for the absorber which must be solved together to obtain the unknown parameters. The solution procedure is discussed in the following section.

3.3 Computational Method:

In a countercurrent absorber, the rich feed gas enters at the bottom and absorbing lean liquid enters at the top of the column and are usually completely specified. However, the lean gas leaves from the top and rich liquid leaves at the bottom, both of which are, at best, partially specified. Therefore, the state of neither end of the column is known completely which leads to a two-point boundary value problem when integrating heat and mass balance equations through the tower. Equations (3.23), (3.30), (3.31), (3.40), (3.41), (3.42), (3.43) and (3.44) give rise to a highly coupled system of equations. For the present case, the packed height was divided into three sections as shown.



Part of the lean liquid, L_1 enters at the top and remaining liquid, L_2 enters after first section of the packing. The lower section is again divided in two parts II & III, to enable redistribution of the liquid. In the present scheme, each section has been divided in 20 equal integration steps giving a total of 60 segments for the total column. This step size is found to be satisfactory since further reduction in size did not significantly change the results. Over each integration step, the thermophysical properties were assumed to remain constant. These properties were updated at the end of each integration step by procedures to be discussed in the next section.

The boundary conditions known at the two ends of the absorber are the

$$\begin{aligned}
 L(Z=H_t) &= L_t \\
 x_1(Z=H_t) &= x_{1t} \\
 x_2(Z=H_t) &= x_{2t} \\
 t(Z=H_t) &= t_t
 \end{aligned}
 \tag{3.45}$$

$$\begin{aligned}
 V(Z=0) &= V_b \\
 y_1(Z=0) &= y_{1b} \\
 y_2(Z=0) &= y_{2b} \\
 T(Z=0) &= T_b
 \end{aligned}
 \tag{3.46}$$

where suffix t denotes tower top and b, tower bottom and H_t is the total packed height of the tower.

Several methods are available for solving two point boundary value problems. For the present work, "Shooting method" has been used (Fox, 1957). In the shooting method, values for the unspecified conditions at the initial point of the interval ("missing initial conditions") are assumed, and the differential equations are numerically integrated to the terminal point by applying essentially an initial value algorithm ("Shooting" at the target terminal points). If the computed terminal values satisfy the specified terminal conditions, the problem has been solved. If they do not, the differences between the computed and specified terminal conditions (the "miss distances") are used to adjust the assumed initial conditions. If the differential equations and boundary conditions are linear, the adjustments need only be made once, but if the differential equations are nonlinear, the adjustment of the missing initial conditions is an iterative process. (Roberts and Shipman, 1972; Fox, 1957; Keller, 1968). In the present case, the differential equations are

coupled. The integration is started from the bottom of the tower with two sets of assumed values for the unknown variables at the tower bottom, i.e., L_b , x_{1b} , x_{2b} and t_b , as well as related concentrations of other components in the liquid x_{3b} , x_{4b} , x_{5b} , x_{6b} for K_2CO_3 , $KHCO_3$, amine and V_2O_5 respectively. The integration is performed using fourth-order Runge-Kutta method. The known boundary conditions at the tower top, i.e., L_t , x_{1t} , x_{2t} and t_t , are then compared with those computed for the two assumed sets. The difference between the known and computed values for the boundary conditions at the top form the difference functioning.

Figure 3.2 shows how the shooting method works. For the liquid flow rate at the bottom, two values L_{b1} and L_{b2} are assumed. The corresponding calculated values $L_{t1,calc.}$ and $L_{t2,calc.}$ are used to calculate the difference functions $L_t - L_{t1,calc.}$ and $L_t - L_{t2,calc.}$ (where L_t is the observed liquid flow rate at the top) which are plotted as A and B. Line AB is extended to intersect x-axis at C which provides the next guess for L_b say L_{b3} . For the next iteration, L_{b2} and L_{b3} are the two values used to get the new guess in the same fashion. The remaining 7 variables, x_{1b} , x_{2b} , x_{3b} , x_{4b} , x_{5b} , x_{6b} and t_b are treated in the same manner.

A computer program has been written in FORTRAN language for DEC 1090 system using above procedure. A brief User's Manual is included in Appendix B.

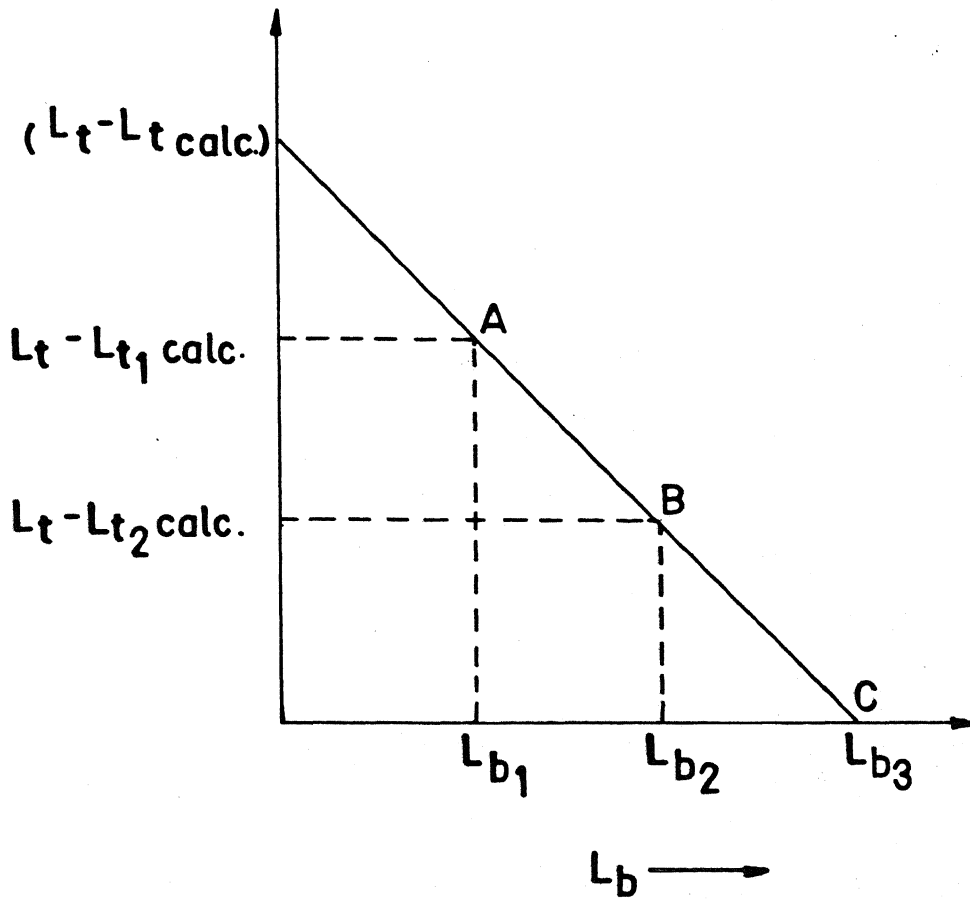


Fig. 3.2 Shooting method

Before we can actually integrate equations (3.23) to (3.44) we need to obtain the thermodynamic properties such as partial pressure, Henry's law constant etc. and transport properties such as viscosity, thermal conductivity and so on. These are discussed in the next section.

3.4 Thermodynamic and Transport Properties:

Evaluation of the requisite thermodynamic and transport properties constitutes a major part of any mathematical modelling effort. Use of appropriate property estimation equations is an integral part of good design program. The original data on vapour-liquid equilibrium for CO_2 -hot carbonate system were published by Benson et al. (1954; 1956), Tosh et al. (1959, 1960). The other physical properties of the system such as density, viscosity, specific heat etc. of the hot carbonate solution were published by Danckwerts & Sharma (1966); Bocard and Maryland (1962), Ratcliff and Holdcroft (1963), Kohl and Risenfield (1979) and others. More recently, Kent and Eisenberg (1975), Savage et al. (1980), and Astarita et al. (1983) have published latest data on thermodynamic and transport parameters. For the gas phase, which is at low reduced pressure and at high reduced temperature, ideal thermodynamics can be used since the compressibility factor is close to unity. In the present case, the criterion is reasonably satisfied and hence ideal thermodynamics have been used to estimate various properties.

The liquid phase properties have been estimated using available correlations or curves as described below.

3.4.1 Vapour-Liquid Equilibrium (VLE):

For the system of CO_2 in $\text{K}_2\text{CO}_3/\text{KHCO}_3$ solution, a single parameter can be defined which completely characterizes the chemical composition of the liquid phase. The parameter chosen for this case is the fractional saturation, x . For an absorption system, x increases along the liquid path in the absorber. If p^* represents the partial pressure of the absorbed component which equilibrates the liquid phase composition; the VLE relationship becomes (Astarita et al. 1983)

$$p^* = A_m'^q F(x, t) \quad (3.47)$$

A' signifies a parameter into which all the activity coefficients are lumped. In spite of this gross simplification, the above equation is usually quite effective in predicting the correct form of VLE relationship. The value of the exponent q in equation (3.47) depends on the stoichiometry of the main reaction involved and $F(x, t)$ is some function of x and t . Actual data on $\text{CO}_2\text{-K}_2\text{CO}_3$ system by Tosh et al. (1959), Bocard and Maryland (1962) and also by Kent and Eisenberg (1975) are well correlated by the following equation suggested by Astarita et al. (1983).

$$p_1^* = 1.95 \times 10^9 \text{ mm}^{0.4} \left(\frac{x^2}{1-x} \right) \exp \left(\frac{-8160}{t} \right) \quad (3.48)$$

where p_1^* , the equilibrium partial pressure of CO_2 , is in atmospheres, m is expressed in kmol/m^3 and t in K. The constant A' in Eq.(3.47) taken here as 1.95×10^9 , can vary in case of very high molarity and especially when the effect of promoter is strong.

For the water vapour a different equation was proposed by Tosh et al. (1959). On the basis of the assumption that the water vapour obeys ideal gas law. The following Clausius-Clapeyron form of equation was put forward by them and was found to correlate their data very well.

$$\log p_2^* = - \frac{L}{(2.303xR)} \left(\frac{1}{t} - 2.45 \times 10^{-3} \right) - 1.1672 + C \quad (3.49)$$

where p_2^* is the equilibrium partial pressure of water vapour in atmospheres; L is the heat of vapourization of water, and C is a constant for a constant molarity or weight percent of K_2CO_3 solution. The heat of vapourization was taken to be 9,800 Kcals/K mole which is close to the average value between 70°C and 130°C obtained from the steam table. The value of C decreases as conversion of K_2CO_3 to KHCO_3 increases and the following expression has been fitted to the data of Tosh et al. by nonlinear regression

$$C = a_c + b_c/x_c + c_c/x_c^2 \quad (3.50)$$

where x_c is the conversion of K_2CO_3 defined as

$$x_c = \frac{0.691(\% \text{ KHCO}_3)}{\% \text{ K}_2\text{CO}_3 + 0.691(\% \text{ KHCO}_3)} \quad (3.51)$$

and a_c , b_c and c_c are regression coefficients.

The total equivalent weight percent K_2CO_3 is defined as

$$\text{Equivalent } K_2CO_3\% = \frac{\%K_2CO_3 + 0.691(\%KHCO_3)}{\%K_2CO_3 + 0.781(\%KHCO_3) + \%H_2O} \times 100 \quad (3.52)$$

For a 30% equivalent K_2CO_3 , a_c , b_c , and c_c were found to be

$$a_c = 1.2014$$

$$b_c = 0.2857$$

$$c_c = -0.0537$$

3.4.2 Henry's Law Constant:

The experimental measurement of the value of Henry's law constant, H , is quite straight forward for a physical solvent; whereas, for a chemical solvent the situation is considerably more complex. Moreover, for an electrolyte solution, the ionic interactions tend to affect its value in a complex way. If H^0 represent the value of the Henry's law constant for pure solvent of a chemically reactive solution (e.g., water, in the case of aqueous solutions), the value of H , for the reactive solution, will usually be of the same order of magnitude as H^0 but appreciably different from it. This is due to the fact that appreciable concentration of the reactive component, usually an electrolyte, increases the "salting out" effect. Van Krevelen and Hoftijzer (1948) and later Danckwerts & Sharma (1966) put forward, on theoretical basis, a correlation as follows:

$$\log \frac{H}{H^O} = K_i I_i \quad (3.53)$$

where I_i = the ionic strength of solution, Kgion/m³

$$= \frac{1}{2} \sum z_i^2 C_i$$

where Z_i = charge of each ionic species

C_i = concentration of each ionic species, Kg-ion/m³

and K_i = a constant that depends only on the nature of the ions present in solution, m³/Kmol.

For the CO₂ - K₂CO₃ system, equation (3.53) applies with

$K_i = 0.062 \text{ m}^3/\text{Kmol}$. For this system, the ionic strength can be related to molarity as

$$I_i = m (3-x) \quad (3.54)$$

and an alternative expression for H in terms of molarity can be written as (Astarita, et al., 1983);

$$\log \frac{H}{H^O} = K_m m \quad (3.55)$$

where $K_m = 0.025 \text{ m}^3/\text{Kmol}$ for CO₂-K₂CO₃ system.

The above equation correlates well, the data given by Kent and Eisenberg (1975) and Astarita et al. and has been used in the present model.

The Arrhenius plot for inverse Henry's law constant of CO₂ in water, i.e., $[H^O]^{-1}$ given by Astarita et al. (1983) has been correlated, for the present work, by linear regression analysis as

$$\log [H^O]^{-1} = a_H + b_H/t \quad (3.56)$$

where a_H and b_H are regression coefficients and have the values -4.3856 and 867.4932, respectively.

3.4.3 Mass Transfer Coefficients:

Several correlations are available for estimation of gas-side mass transfer coefficient. Van Krevelen and Hoftijzer (1948), Danckwerts (1970), and Uchida et al. (1972) have reported a number of such correlations. Astarita et al. (1983) have recommended the following correlation proposed by Onda et al. (1968), which has been used in the present model.

$$\frac{k_{gk} R T}{a D_{gk}} = C' \left(\frac{\tilde{G}}{a \mu_g} \right)^{0.7} \left(\frac{\mu_g}{\rho_g D_{gk}} \right)^{1/3} (a d_p)^{-2.0} \quad (3.57)$$

where the subscript g refers to properties in the gas phase, \tilde{G} is the mass flow rate of inert gas in $\text{Kg}/(\text{m}^2)(\text{hr})$, d_p is the packing size, and C' is a dimensionless constant which depends on the size of packing. For the present case, where 1.5" Intalox saddles have been used, C' is taken as 5.28. R is the universal gas constant in $(\text{m}^3)(\text{atm})/(\text{Kmol})(\text{K})$, μ_g , ρ_g and D_{gk} are the viscosity, density and diffusivity of the k th component respectively in the gas phase. In this case $d_p = 0.0115$.

The liquid side mass transfer coefficient is obtained from the analysis of Van Krevelen and Hoftijzer (1948) as follows:

$$\frac{k_L (\frac{\mu^2}{g \rho^2})^{1/3}}{D} = 0.015 (\frac{\tilde{L}}{a \mu})^{2/3} (\frac{\mu}{\rho D})^{1/3} \frac{(\frac{\mu^2}{g \rho^2})^{1/3} (\frac{k_{II} C_R}{D})^{1/2}}{\tanh (\frac{\mu^2}{g \rho^2})^{1/3} (\frac{k_{II} C_R}{D})^{1/2}} \quad (3.58)$$

where \tilde{L} = liquid flow rate, $\text{kg}/(\text{m}^2)(\text{sec})$

g = acceleration due to gravity, m/sec^2

ρ = liquid density, Kg/m^3

μ = liquid viscosity, $\text{kg}/(\text{m})(\text{sec})$

D = liquid diffusivity, m/sec^2

k_{II} = reaction rate constant, $\text{kmol}/(\text{m}^3)(\text{sec})$

C_R = average concentration of active component,
 kmol/m^3

Experimentally it was found that the above semiempirical equation is a satisfactory approximation for the correlation of the data.

The overall mass transfer coefficient for the absorbed component CO_2 consists of the gas and liquid side mass transfer coefficients and is expressed as

$$\frac{1}{K_{g1}} = \frac{1}{k_{g1}} + \frac{H}{k_{l1}} \quad (3.59)$$

where H is obtained from equation (3.55).

It may be assumed that there is no liquid side resistance for the mass transfer of the solvent water vapour. Therefore, the overall mass transfer coefficient for the solvent water vapour is

$$K_{g2} = k_{g2} \quad (3.60)$$

3.4.4 Heat Transfer Coefficient:

Due to lack of experimental data on gas-liquid heat transfer coefficient in packed column, Uchida et al. (1972) have recommended that the analogy between the heat and mass transfers can be used to calculate heat transfer coefficient, h , in the packed column. Thus

$$j_H = j_D \quad (3.61)$$

where j_H = j factor for heat transfer

and j_D = j factor for mass transfer

By definition,

$$j_H = \frac{h}{C_{pg} \rho_g v} \left(\frac{\mu_g C_{pg}}{\lambda_g} \right)^{2/3} \quad (3.62)$$

and

$$j_D = \frac{k_{gk}}{v} \left(\frac{\mu_g}{\rho_g D_{gk}} \right)^{2/3} \quad (2.63)$$

where suffix k denotes the k th component transferred from gas to liquid.

Combining (3.61), (3.62) and (3.63) we get,

$$h_k = k_{gk} \left(\frac{\lambda_g^2 C_{pg}}{\rho_g D_{gk}^2} \right)^{1/3} \quad (3.64)$$

where C_{pg} = specific heat of gas mixture, Kcal/(Kg)(K)

λ_g = thermal conductivity of gas mixture, Kcal/(hr)(m)(K)

Equation (3.64) has been used in the present model to compute component heat transfer coefficients. Overall heat transfer coefficient, h , for the gas mixture has been obtained by taking the molar average of component coefficients. The experiments performed by Heertjes and Ringens (1956) and Lynch and Wilke (1955) show the validity of this relation.

3.4.5 Wetted Interfacial Area:

Usually, interfacial area reported for various sizes of the dry packing is different from the gas-liquid interfacial area of the wetted packing, that is actually available for mass transfer. Van Krevelen and Hoftijzer (1948), Danckwerts (1970), Puranik and Vogelpohl (1974) and Laurent and Charpentier (1974) have discussed the estimation of wetted interfacial area. For the sake of simplicity we use the correlation proposed by Van Krevelen and Hoftijzer given as follows:

$$\ln \frac{a_d - a}{a_d} = -C_a \frac{\tilde{L}}{\rho} \quad (3.65)$$

where a_d = dry packing surface area, m^2/m^3

a = wetted interfacial area, m^2/m^3

\tilde{L} = liquid mass flow rate, $Kg/(sec)(m^2)$

ρ = density of liquid, Kg/m^3

$C_a = 5000.0$

The same interfacial area has been used for heat transfer also.

3.4.6 Density of Liquid and Gas:

Bocard and Maryland (1962) and Kohl and Risenfield (1979) have reported specific gravity data of aqueous solutions for different equivalent weight percent K_2CO_3 at different temperatures. Following relation has been obtained by linear regression of the data of Bocard and Maryland both with respect to temperature and concentration, which is valid for temperature range of 70 to 130°C and 20 to 40 weight percent total equivalent K_2CO_3 .

$$s = a_s + b_s w - c_s t_C \quad (3.66)$$

where s = specific gravity of K_2CO_3 solution

w = total equivalent weight percent K_2CO_3

t_C = liquid temperature, °C

a_s, b_s and c_s are regression constants with the following values

$$a_s = 1.0679$$

$$b_s = 0.01$$

$$c_s = 9.7 \times 10^{-4}$$

The density of the gas mixture is calculated from the ideal gas law as

$$\rho_g = \frac{P M_g}{RT} \quad (3.67)$$

where ρ_g = density of the gas mixture, Kg/m^3

P = total tower pressure, atm

M_g = molecular weight of the gas mixture

R = universal gas constant = $0.08205 \text{ m}^3 \text{ atm}/(\text{K})(\text{Kmol})$

T = gas temperature, K

3.4.7 Viscosity of Liquid and Gas:

Data on the viscosity of aqueous K_2CO_3 - KHCO_3 solutions has been given by Bocard and Maryland (1962). The variation of viscosity has been reported both with respect to temperature and weight percent K_2CO_3 total equivalent. For the present case of 30 weight percent K_2CO_3 , the following relationship has been developed by non-linear regression and used in the model

$$\mu = a' + b't_F + c't_F^2 + d't_F^3 \quad (3.68)$$

where μ = viscosity of liquid in $\text{Kg}/(\text{m})(\text{hr})$

t_F = liquid temperature, $^{\circ}\text{F}$

and a', b', c' and d' are the regression constants with the following values:

$$a' = 12.9275$$

$$b' = -0.1114$$

$$c' = 4.1184 \times 10^{-4}$$

$$d' = -5.796 \times 10^{-7}$$

The viscosities of the individual gas components at atmospheric pressure, averaged over the temperature range of $70 - 135^{\circ}\text{C}$ have been obtained from Perry (1973). The mixture viscosity is obtained by using the correlation of Wilke (Reid et al., 1977) given as follows:

$$\mu_g = \frac{\sum_{i=1}^n \frac{y_i \mu_{gi}}{\sum_{j=1}^n y_j \phi_{ij}}}{n} \quad (3.69)$$

where μ_g = viscosity of the gas mixture

μ_{gi} and μ_{gj} are the viscosities of i th and j th components respectively in the gas phase

y_i and y_j are the mole fractions of i th and j th components respectively in the gas phase

$$\text{and } \phi_{ij} = \frac{1 + (\mu_{gi}/\mu_{gj})^{1/2} (M_j/M_i)^{1/4}}{8(1 + M_i/M_j)^{1/2}} \quad (3.70)$$

i and j refer to i th and j th components respectively.

Since at high reduced temperatures or low reduced pressures the viscosity of a gas does not vary significantly from its low pressure value, there is no need to incorporate pressure correction for the mixture viscosity given by equation (3.69).

3.4.8 Diffusivities of Liquid and Gas:

Danckwerts and Sharma (1966) and Ratcliff and Holdcroft (1963) provided early correlations of diffusivity of dissolved carbon dioxide in solvents at different temperatures. Savage et al. (1980) have given more recent data on diffusivity of values for $\text{CO}_2\text{-K}_2\text{CO}_3$ system. For each of computer calculations, the following correlation has been developed by means of linear regression analysis of their data

$$\log D = a_D - b_D/t - 0.4437 \quad (3.71)$$

where D = liquid diffusivity (assumed equal for all components),
 m^2/hr

a_D and b_D are regression constants with following values

$$a_D = -3.0188$$

$$b_D = 586.9727$$

The binary gas diffusivities are obtained using the following correlation proposed by Sherwood and Pigford (1952)

$$D_{kj} = (2.6544 \times 10^{-4}) \frac{T^{3/2}}{P(V_k^{1/3} + V_j^{1/3})^2} \sqrt{\frac{1}{M_k} + \frac{1}{M_j}} \quad (3.72)$$

where D_{kj} = binary diffusivity in gas phase, m^2/hr

V_k, V_j = molecular volumes of k and j

The mixture diffusivity has been calculated using the simplified correlation suggested by Reid et al. (1977) as follows:

$$D_{gk} = \left(\sum_{\substack{j=1 \\ j \neq k}}^n \frac{y_j}{D_{kj}} \right)^{-1} \quad (3.73)$$

where D_{gk} is the diffusivity of the k th component in the gas mixture, m^2/hr .

3.4.9 Specific Heat of Liquid and Gas:

Data on the specific heat of K_2CO_3 solution were published by Kohl and Risenfield (1979). The accuracy of these data has been reported to be ± 0.0024 Kcal/Kg K. These data have been well correlated by the following equation and used in the present model.

$$C'_{pL} = a'' + b''w + c''w^2 + d''w^3 \quad (3.74)$$

where C'_{pL} = specific heat of liquid, Kcal/(Kg)(K)

a'' , b'' , c'' and d'' are regression coefficients with values,

$$a'' = 0.9998$$

$$b'' = -0.00914$$

$$c'' = -0.1063 \times 10^{-3}$$

$$d'' = 0.3058 \times 10^{-5}$$

The value of the specific heat of liquid in Kcal/(Kmol)(K), i.e. C_{pL} , is obtained by multiplying C'_{pL} by the molecular weight of the liquid solution. Average specific heats of the individual gas components for the temperature range 70 - 135°C have been obtained from the nomograph given in Perry (1973).

The specific heat of the gas mixture has been calculated assuming the mixture to be an ideal one by

$$C_{pg} = \sum_{i=1}^n y_i C_{pgi} \quad (3.75)$$

where C_{pgi} = average specific heat of i th component in the gas mixture, Kcal/Kmol/K

3.4.10 Thermal Conductivity of the Gas Mixture:

The average thermal conductivity of the individual gas components for the temperature range 70°C - 135°C have been obtained from the nomograph of Chang (Reid et al., 1977). The thermal conductivity of the gas mixture is obtained by using

the Wassiljewa equation (Reid et al., 1977) given below:

$$\lambda_g = \frac{\sum_{i=1}^n \frac{y_i \lambda_{gi}}{\sum_{j=1}^m y_j A_{ij}}}{\sum_{j=1}^m y_j A_{ij}} \quad (3.76)$$

where λ_{gi} = thermal conductivity of pure component i in the gas mixture

A_{ij} = is found by theoretical analysis to be same as ϕ_{ij} equation (3.70)

3.4.11 Heat of Absorption

Absorption of CO_2 in K_2CO_3 solution is accompanied by two heat effects, the heat of solution and heat of reaction. The net heat of absorption has been correlated from the data of Bocard and Maryland (1962) by non-linear regression. Following relation has been obtained.

$$\Delta H_1 = a_h + b_h w + c_h w^2 + d_h w^3 + e_h w^4 \quad (3.77)$$

where ΔH_1 = net heat of absorption of carbon dioxide in hot potash solution, Kcal/Kmol

a_h, b_h, c_h, d_h and e_h are the regression constants with the following values

$$a_h = 6510.8058$$

$$b_h = 19.4580$$

$$c_h = 1.2727931$$

$$d_h = -0.0313384$$

$$e_h = 3.955 \times 10^{-4}$$

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3.5 Effect of Rate Promotion on VLE and Kinetics:

In Section 2.3 it was discussed how the rate of CO_2 absorption is promoted by addition of amines to the K_2CO_3 solution. These amines affect the vapour-liquid equilibrium and the kinetics of the overall reaction in a complex way. The amine can act as a base or it can form carbamates for which the chemistry is even more complex. For a base promoted solution, where carbamate formation is either neglected or considered to be an unstable process, the protonation constant of the base B is given as

$$K_P = \frac{[B][H^+]}{[BH^+]} \quad (3.78)$$

where $[B]$ = concentration of free base, Kmol/m^3

$[H^+]$ = concentration of hydrogen ion, K ion/m^3

$[BH^+]$ = concentration of protonated base units, Kmol/m^3

The amine is a weaker base than the carbonate and hence its protonation constant K_P is larger than the second dissociation constant, K_{C_2} of carbonic acid

$$K_{C_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (3.79)$$

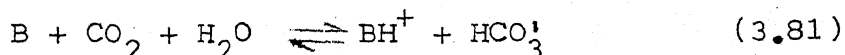
where $[CO_3^{2-}]$ = concentration of carbonate ion, K-ion/m^3

$[HCO_3^-]$ = concentration of bicarbonate ion, K-ion/m^3

Therefore, the following reaction



is displaced to the left. Hence as long as x does not approach the value of unity, the base will remain essentially in its undissociated form B (Astarita et al., 1983). Reaction (2.5) is still the main reaction, and the value of p_1^* will essentially be same as in an unpromoted solution given by equation (3.48). At values of x very close to unity, the $[\text{HCO}_3^-] / [\text{CO}_3^{2-}]$ ratio will become quite large and BH^+ will begin to form, i.e., the base will begin to exhibit its ability to react with carbon dioxide according to the following reaction



Values of x in excess of unity can be achieved in this case. Astarita et al. (1983) have proposed the following rough rule of thumb.

- i) When $x < 1$, the main reaction is (2.5) and the base (amine in present case) acts simply as a catalyst. The VLE relationship is unchanged and given by eqn. (3.48).
- ii) When $x \geq 1$, the main reaction is (3.81) and the base acts as a chemical sink for CO_2 and the VLE relationship has to be changed as follows:

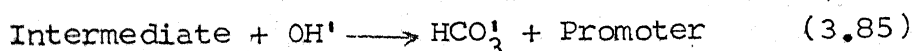
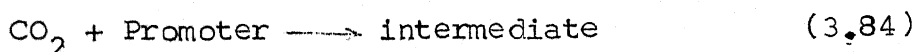
$$p^* = \frac{H K_p}{K_{C_1}} m \frac{(x-1)(1+x)}{c + 1-x} \quad (3.82)$$

where m_c is the total amount of amine added to the solution and K_{C_1} is the first ionisation constant for carbonic acid and is given by

$$K_{C_1} = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (3.83)$$

In the present case, x varied from about 0.2 to 0.67 along the liquid path of the tower and hence we can safely neglect equation (3.81) and consider case i) to be valid. Therefore, VLE relationship given by equation (3.48) holds good.

To see how the kinetics is affected by the presence of amine, we consider the shuttle mechanism once again (discussed earlier in Section 2.3).. The shuttle mechanism involves the following two chemical steps,



Since these two reactions take place at the interface and in the bulk respectively they are, therefore, separated by the diffusion processes. In absence of diffusion processes, the sequence (3.84) and (3.85) is a classical sequence of homogeneous catalysis. Therefore the amine promoter that acts via a shuttle mechanism at low temperature may well act as a homogeneous catalyst at higher temperature, where reaction (3.85) may be fast enough to take place at the interface region.

If the amine promoter is regarded as a homogeneous catalyst as suggested in case i), its largest possible effect

is to speed up the rate of reaction (2.5) to the point where mass transfer takes place in the instantaneous reaction regime. As the ratio of diffusion time to reaction time is much greater than unity (about 10^4), for the unpromoted solution in the present case, the reaction is fast enough to result in significant rate enhancement; and, on being promoted, the rate promotion factor E is most likely to reach its maximum value, defined as

$$E_{\max} = \frac{I_{\infty}}{I_{\text{unpromoted}}} \quad (3.86)$$

where I_{∞} is the enhancement factor in the instantaneous regime and $I_{\text{unpromoted}}$ is that for the unpromoted solution. Hence the effective rate enhancement factor for the present case is

$$I_{\text{promoted}} = E_{\max} \times I_{\text{unpromoted}} = I_{\infty} \quad (3.87)$$

The value of I_{∞} has already been given by equation (3.20)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Calculated Results and Model Validation:

The model presented in the previous chapter has been tested for carbon dioxide absorber in an existing ammonia plant. The plant uses hot potassium carbonate solution with diethanolamine (DEA) promoter for absorption of carbon dioxide. The packed absorber has three sections. The lean solution from the regenerator is split into two parts. One part enters the absorption tower at the top after being cooled, whereas, the other part enters after the first section of the packing (see figure in Section 3.3). Table 4.1 shows the design parameters for the absorption tower. Table 4.2 shows the value of the input and output variables such as flow rates of liquid and gas streams, the composition of each stream, temperature etc. Also shown in Table 4.2 are the calculated values for the same outlet variables for comparison.

Except for the mole fraction of water vapour in the gas phase, all the calculated liquid and gas compositions match well with the plant values very well, the maximum deviation being 7 percent for the carbon dioxide. Even this 7 percent deviation may be due to measurement error since there is a higher uncertainty in measurement for small concentration range. If we calculate the percent CO_2 removed

Table 4.1: Design Parameters for the Absorber

Height of Packing:

i) 1st section	:	6.0 m
ii) 2nd section	:	5.6 m
iii) 3rd section	:	5.6 m
Dia. of packed bed	:	1.4 m
Packing size and material:	37 mm (1.5") Ceramic Intalox saddles	

Table 4.2: Comparison of Calculated Results
with the Observed Plant Data

Parameters	Inlet	Outlet		
		Observed	Calculated	%Deviation
Liquid flow rate, Kmol/hr	2629.8357	5308.0	5351.690	-0.82
Liquid temperature, K	343.0	392.0	390.0	0.50
Liquid composition:				
i) Mole fraction of K_2CO_3	0.04013	0.0158	0.0159	-0.63
ii) Mole fraction of $KHCO_3$	0.02015	0.0663	0.0669	-0.90
iii) Mole fraction of water	0.9320	0.9198	0.9095	1.12
iv) Mole fraction of DEA	7.193×10^{-3}	7.0053×10^{-3}	7.070×10^{-3}	-0.92
v) Mole fraction of V_2O_5	5.554×10^{-4}	5.399×10^{-4}	5.449×10^{-4}	-0.93
Gas flow rate, Kmol/hr	762.877	547.090	544.690	0.43
Gas temperature, K	408.0	-	382.2	-
Gas composition:				
i) Mole fraction of CO_2	0.1659	0.001	0.00107	-7.0
ii) Mole fraction of CH_4	0.00184	0.00257	0.00258	-0.39
iii) Mole fraction of CO	0.00263	0.00366	0.00368	-0.55
iv) Mole fraction of H_2	0.5306	0.7388	0.7431	-0.58
v) Mole fraction of N_2	0.1733	0.2413	0.2427	-0.58
vi) Mole fraction of Ar	0.0021	0.0029	0.00292	-0.69
vii) Mole fraction of	0.1237	0.0099	0.0058	41.40

then the observed value is 99.4 which is to be compared with the calculated value of 99.36. The calculated value of mole fraction of water vapour in the gas was 41.4% lower than the plant data. While the actual reason for this discrepancy is unknown, it may be because of the vapour-liquid equilibrium data (Tosh et al., 1959) which are old and may be in error. Again if we consider the percent removal of water vapour in the column then the observed value is 92% which must be compared with the calculated value of 95.3% and now the match looks more reasonable. The flow rates and temperatures of both gas and liquid streams match well. Since most of the data match quite closely with the calculated values, it can be concluded that the model is satisfactory.

To establish the generality of the model developed in the present work, it is necessary to validate it against several sets of plant data preferably in different regions of temperature, flow rates, etc. However, getting such actual data is not easy and in the present case, only one set of data could be obtained.

4.2 Calculated Profiles:

The temperature, flow and concentration profiles have been calculated using the model along the packed tower height from the bottom to the top. A typical set of profiles are shown in Figures 4.1 and 4.2 for the data set given in

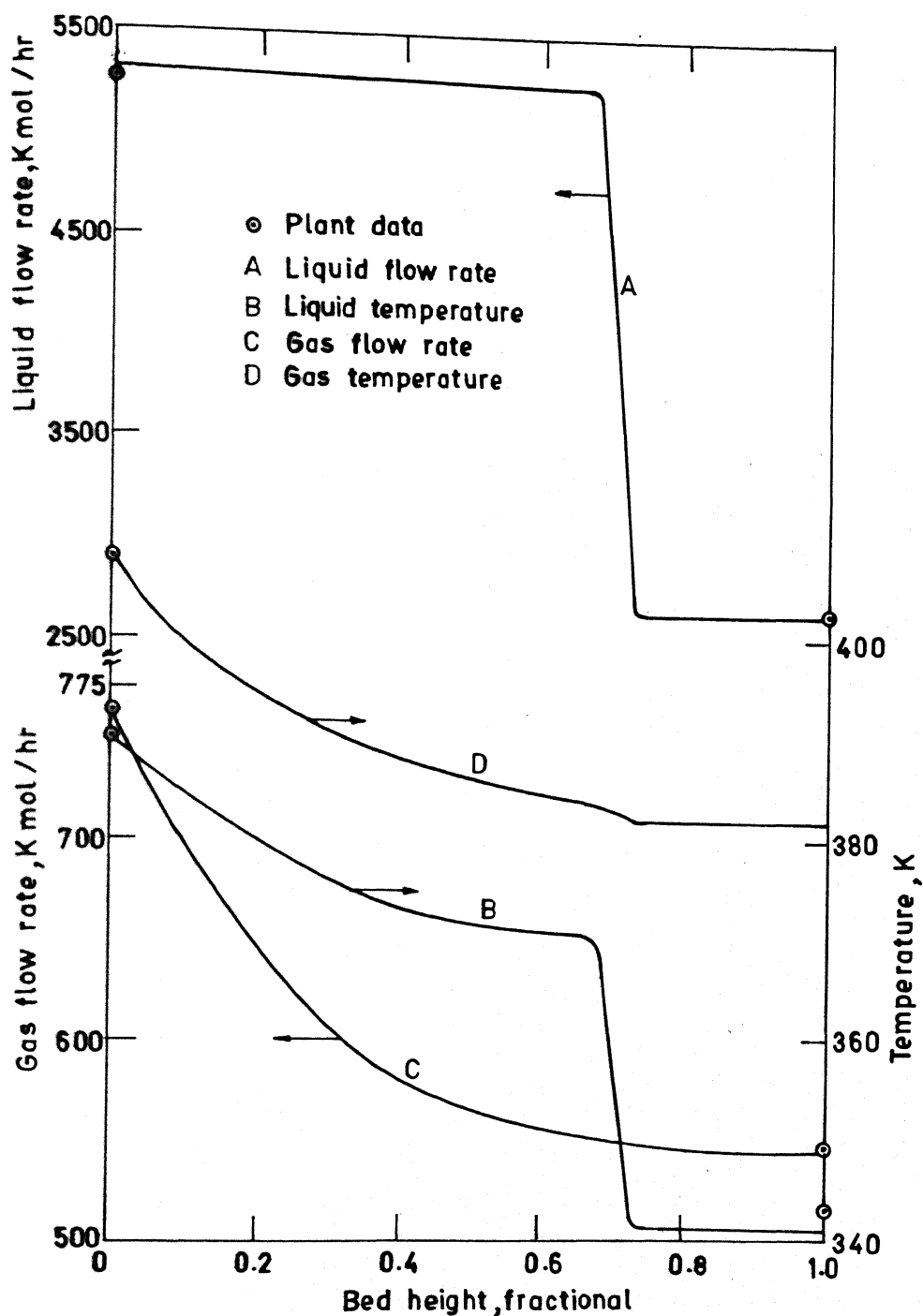


Fig. 4.1 Temperature and flow profiles in the absorber

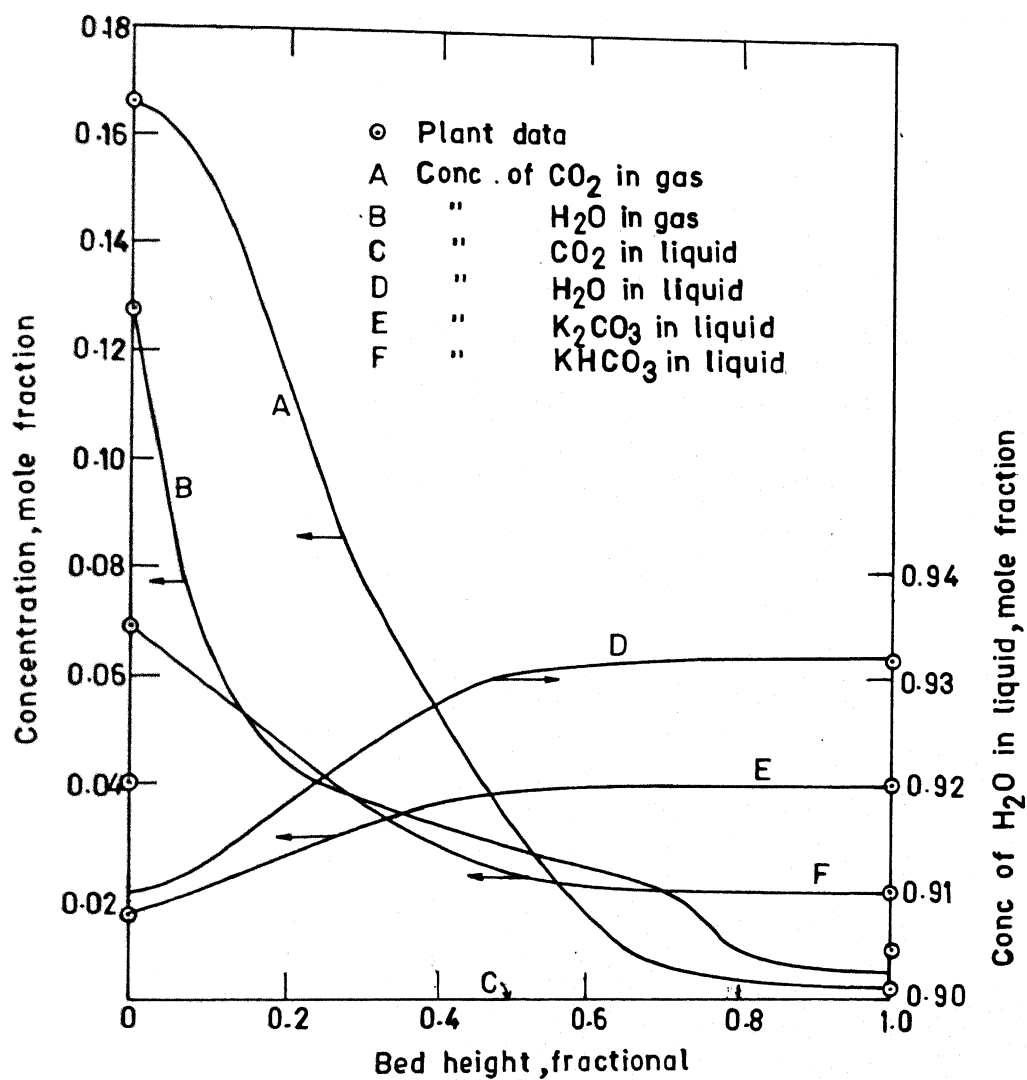


Fig. 4.2 Concentration profiles in the absorber

Tables 4.1 and 4.2. The step change in liquid flow rate and liquid temperature seen in Figure 4.1 is because of the addition of split stream of lean absorbent at the end of first section of packing. While the gas flow rate is not affected by the liquid addition, the gas temperature shows a slight increase. Since the bed height is measured from bottom up, the addition of liquid shows a step decrease when the x coordinate changes from 0 to 1. Gas flow rate decreases along the height because of absorption of CO_2 and water vapour. The gas temperature decreases as it moves up the column since heat is being transferred to liquid because of absorption and temperature difference. For the same reasons, liquid temperature increases as it moves down the column.

The concentration profiles for various components are shown in Fig. 4.2. The concentrations of CO_2 and water vapour in gas phase decrease as the gas moves up the column. Since CO_2 reacts with K_2CO_3 there is no free carbon dioxide in the liquid phase. Concentration of K_2CO_3 in the solution decreases as it moves down the column since it reacts with the dissolved CO_2 . As the reaction product is KHCO_3 , its concentration increases as the liquid travels towards the bottom.

4.3 Sensitivity Analysis:

From a plant operator's point of view, it is important to know how sensitive is the absorption process with respect

to certain operating variables. In the present case where the objective is to remove CO_2 from the synthesis gas, one would like to find how the exit stream CO_2 concentration would vary if the operating pressure of the tower was to change from its design value. Figure 4.3 shows this result. A decrease of 5 atms in total pressure could significantly lower the CO_2 removal efficiency. Figure 4.4 shows how exit CO_2 concentration would change if the fraction of lean absorbent fed at the top of the column is varied from its design value. This is a less sensitive parameter compared to the total pressure, but, an increase in this stream will result in a higher purity of synthesis gas. Changing the temperature of cold lean stream fed at the top of the tower seems to have very little effect on CO_2 removal (Figure 4.5, curve A). This is because in the low temperature range, VLE is not significantly affected by temperature variation. Also the amine promotion is negligible at low temperatures. However, an increase in temperature of the split stream lean absorbent adversely affects the gas purity as seen from curve B in the same figure.

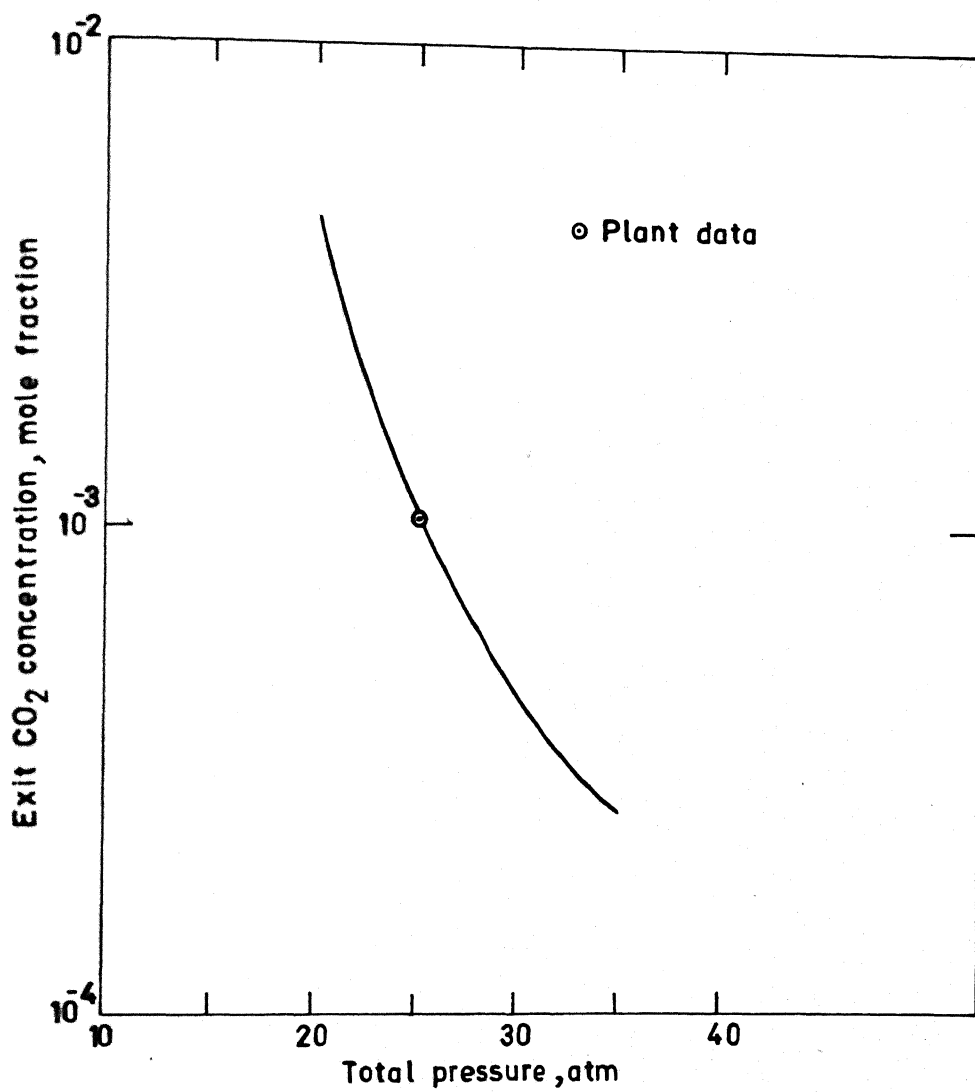


Fig. 4.3 Exit CO₂ concentration Vs. total pressure

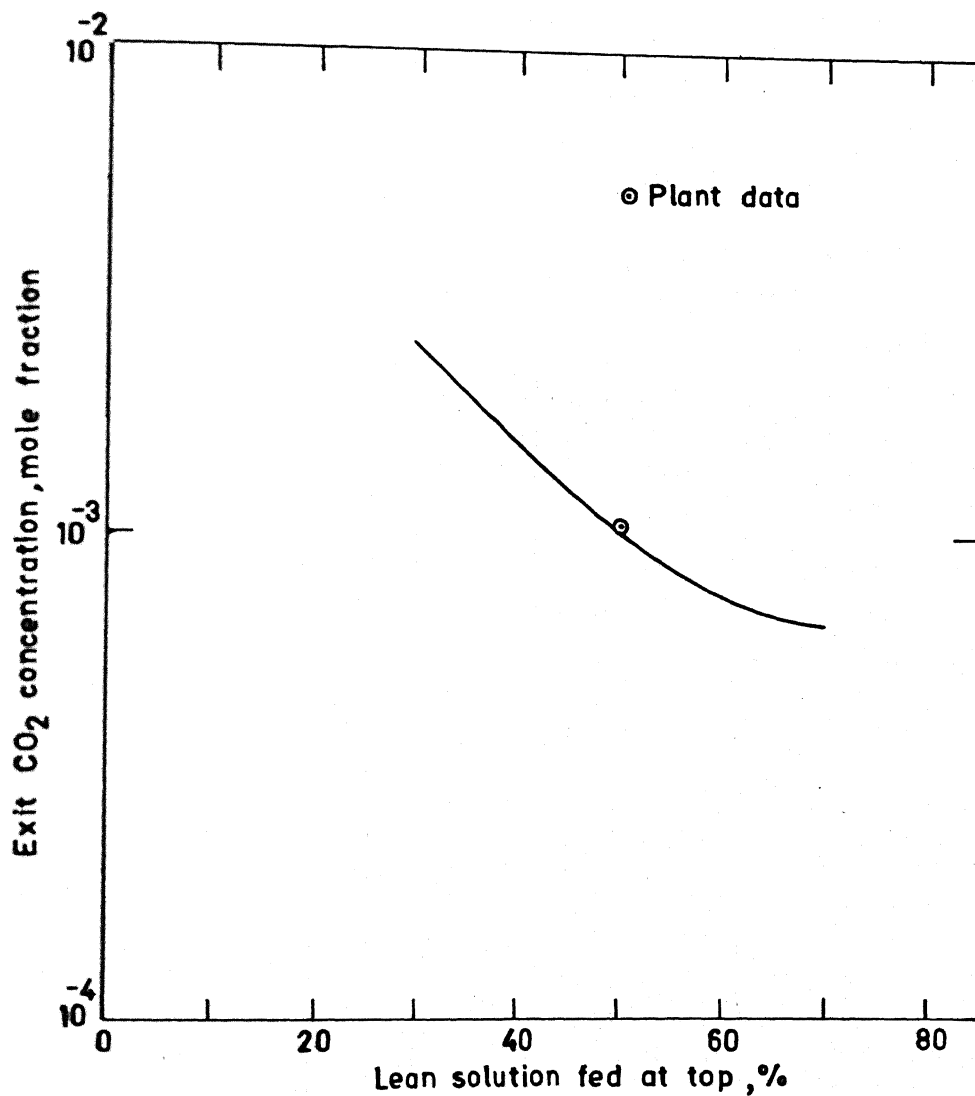


Fig. 4.4 Exit CO₂ concentration Vs percent lean solution fed at the top

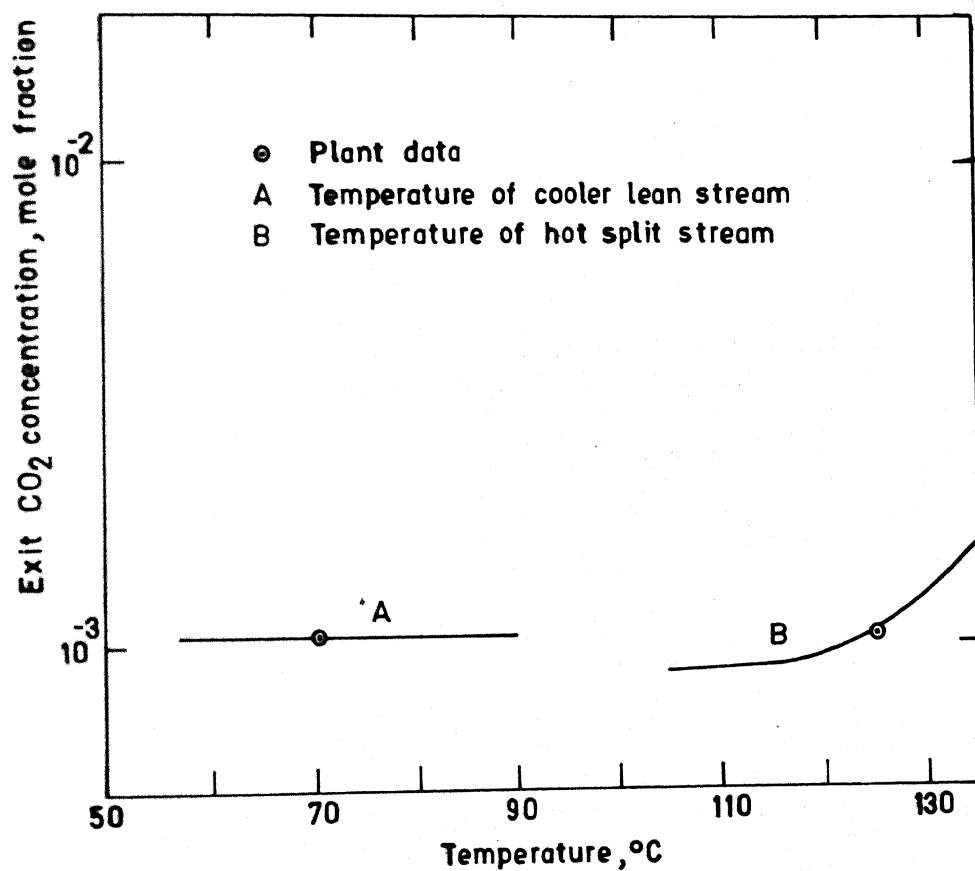


Fig.4.5 Exit CO₂ concentration Vs. temperature of lean streams

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The model of CO_2 absorber, developed in the present study, adequately accounts for the effect of presence of amines in the hot carbonate solution. While amine seems to play the role of a catalyst and pushes the CO_2 - K_2CO_3 reaction to the instantaneous regime, the promotional effect in modelling the VLE curve is negligible. A close agreement between the calculated values and experimental results for one set of plant data justifies the assumptions made. However, in absence of extensive testing of the model, its generality can not be established.

In the present study, only the absorption unit has been modelled. However, it is desirable to model the complete Benfield system which includes a regenerator and a few heat exchangers in addition to the absorber. Since several industrial units use promoters other than amines, it may be desirable to study their effects on CO_2 absorption.

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APPENDIX A

ESTIMATION OF REACTION RATE CONSTANT

The kinetic constant in dilute, unpromoted solution at low temperature is given by

$$\log k_{II_{\text{infinite dilution}}} = 13.635 - 2895/t \quad (\text{A.1})$$

which correlates the infinite dilution data very well in the range $0^\circ - 40^\circ\text{C}$. At room temperature, the reaction rate constant, is a strong function of ionic strength and is related to its value at infinite dilution as

$$\log k_{II_{\text{infinite dilution}}} = 0.08I_i \quad (\text{A.2})$$

The activation energy is same as that at infinite dilution.

The following equation for k_{II} is reasonably well established and can be used with confidence at all ionic strengths of interest, as well as, in the temperature range of $0^\circ - 110^\circ\text{C}$,

$$\log k_{II} = 13.635 - \frac{2895}{t} + 0.08 I_i \quad (\text{A.3})$$